

## Pyrolysis of Phenyl Acetate: a Concerted Reaction

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A kinetic study reveals that the unimolecular decomposition of phenyl acetate into phenol and ketene occurs concertedly, probably *via* a four-centre cyclic transition state.

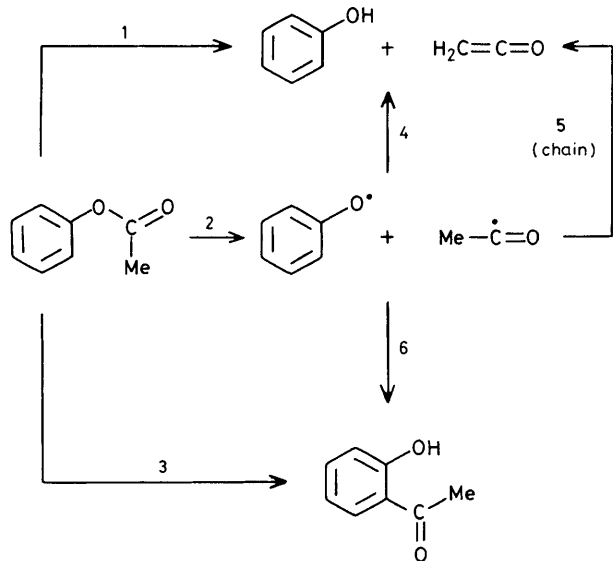
Phenyl acetate and other aryl esters undergo a variety of reactions following thermal or photochemical excitation. Thus pyrolysis of phenyl acetate results in the formation of phenol and ketene<sup>1</sup> but u.v. irradiation in the liquid phase leads to phenol and hydroxyacetophenones.<sup>2</sup>

The possible competition between free radical and concerted processes in these systems has received considerable attention.<sup>3,4</sup> Although schemes based on radical species are admittedly able to account for all these facts, steps 2, 4 (or 5), and 6 (Scheme 1), it is also true that the alternative concerted pathways, steps 2 and 3 (the Fries rearrangement) cannot be definitely ruled out from available evidence. Both mechanisms have in fact been proposed for the thermal decomposition of phenyl acetate. In contrast with earlier suggestions of a free

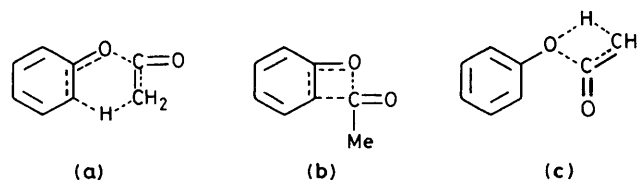
radical chain (steps 2 and 5),<sup>1</sup> Meyer and Hammond favoured a concerted reaction (step 1) based on their inability to detect ketene in the gas-phase photolysis of phenyl acetate, a system which certainly involves radical intermediates.<sup>3</sup> Later reports have rejected this argument, however, since the pyrolysis of  $\text{PhOCOD}_3$  does not lead to incorporation of deuterium into the aromatic ring,<sup>5</sup> as required by the six-centre transition state put forward by Hammond (Scheme 2, a).

In order to clarify the issue we have now undertaken a kinetic study of the pyrolysis of phenyl acetate at very low pressures, conditions which effectively isolate the primary step. The technique, which has been described in detail elsewhere,<sup>6</sup> involves a heatable molecular flow reactor operating at very low pressures. The reactant becomes thermalized in a few gas-wall collisions and subsequently undergoes unimolecular decomposition in the fall-off region. Products, radical or otherwise, escape the reactor before engaging in bimolecular reactions and are directly analysed by an on-line mass spectrometer.

Below 950 K no changes in the mass spectrum of phenyl acetate were observed. Between 950 and 1120 K the intensity of the molecular ion of phenyl acetate,  $m/z = 136$ , decreased owing to decomposition whereas those at  $m/z$  94 (PhOH) and 42 ( $\text{CH}_2=\text{C}=\text{O}$ ) steadily increased. Since the hydroxyacetophenones display a distinctive fragment  $(M-15)^+$  at  $m/z$  121,<sup>7</sup> their formation would have been detected easily. Therefore, the uncatalysed gas-phase thermal Fries rearrangement which would proceed through transition state b (Scheme 2) does not occur. A tenfold reduction of the flow rate of reactant down to



Scheme 1



Scheme 2

$10^{13.5}$  molecules/s did not modify the observed mass spectral pattern. Under these conditions it can be shown that even the fastest bimolecular reactions become much slower than escape from the reactor. Moreover, any acetyl radicals, possibly formed by bond fission (step 2) would be expected to decarbonylate rather than disproportionate with phenoxyl radicals (step 4).<sup>2</sup> From this evidence we conclude that phenol and ketene are indeed the products of a concerted reaction.

From measured rates for reaction (1) and an estimated high-pressure  $A$ -factor<sup>8</sup>  $A_1 = 10^{12.8} \text{ s}^{-1}$ , standard Rice–Ramsperger–Kassel–Marcus (R.R.K.M.) calculations<sup>9</sup> lead to the expression  $\log(k_1/\text{s}^{-1}) = 12.8 - 55.9/\theta$  ( $\theta = 2.3 \times R = 4.575 \times 10^{-3} T \text{ kcal/mol}$ ) (1 cal = 4.184 J). Although these experiments do not specifically probe into the detailed structure of the transition state involved, it is clear that present results definitely rule out a chain mechanism. In addition, if we choose to accept the evidence derived from labelling experiments<sup>5</sup> as genuine, then a six-centre cyclic transition state can also be excluded. On the other hand, a four-centre concerted reaction leading to [ $O\text{-}^2\text{H}$ ]phenol in the pyrolysis of  $\text{PhO-COCD}_3$  accounts for all facts (Scheme 2,c).

Summing up: (i) the lowest energy path for thermal decomposition of phenyl acetate and, by extension, of aryl esters possessing hydrogen atoms  $\beta$  to the carbonyl group is a four-centre concerted reaction producing phenol and ketene; (ii) no concerted homogeneous thermal process involving ring attack with formation of cyclohexadienones *via* transition

states (a) and (b) in Scheme 2 seems to be allowed in aryl esters;<sup>9</sup> (iii)  $k_1$  at 1000 K indicates a reaction that is about 10 times faster than bond fission<sup>10</sup> ( $\log k_2 = 15.3 - 72.3/\theta$ ) and step 1 would not compete favourably with olefin elimination in alkyl esters, since the  $E_1$  value of 55.9 kcal/mol is about 8 kcal/mol larger than the activation energies of the associated six-centre transition states.<sup>8</sup>

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